Calculation of energies of the isoelectronic series of atoms ($Z \leq 29$) using the Hartree–Fock method

I N Eremkin[1], Yu B Malykhanov[2] and M V Gorshunov[2]
[1]ANO Center for Professional Training, Saransk 430003, Russia
[2]M.E. Evsev'ev Mordovian State Pedagogical Institute, Saransk 430007, Russia

E-mail: eryomkin@mail.ru

Abstract. Energy of atoms from hydrogen to cuprum and all their ions up to the one-electron atom that were calculated in the algebraic approximation of the Hartree–Fock method were compared with the experimental values obtained from ionization potentials. It was established that the calculated energies of atoms with $Z \leq 29$ were only 0,3-1,0% greater than the experimental values. This indicated that the approximations underlying the Hartree–Fock method were correct.

1. Introduction

Knowledge of the energies of ionized states in addition to the ground-state energy is necessary in several areas of physics. In particular, highly ionized atoms play an important role in plasma physics. The ground-state energy of atoms and also of their ions can be found experimentally if ionization potentials for all of them up to the one-electron atom are measured. In turn, measurement of the last from atomic spectra is a complicated problem in atomic spectroscopy. Ionization potentials of all atoms in the Periodic Table were found through multi-year atomic spectroscopy studies [1, 2]. However, only first ionization potentials were measured for heavy atoms ($Z \geq 30$). Therefore, theoretical calculation of the energies of atoms and ions based on one quantum-mechanical approximation method or another is critical. Energies of light atoms are currently calculated with sufficiently high accuracy using variational methods and methods that take into account correlation [3]. However, the calculation of energies of heavy atoms in such an approximation is a complicated problem so that calculations of such atoms can be performed in practice using, for example, the Hartree–Fock (HF) method [4, 5]. The HF method was created in order to calculate the energies of atoms and ions [4]. However, it is approximate in nature because it is based on a one-electron approximation. An additional simplification, an approximation of the central field that enables radial and angular parts to be separated in one-electron functions, is used for atoms in the framework of this method. The HF equations for any atomic configurations can be solved by a numerical method [4] and in the framework of an algebraic approach [5-9] owing to these simplifications. Herein energies of the first 29 atoms of the Periodic Table and all their ions up to the one-electron atom inclusive are calculated using the algebraic approximation of the HF method.

All ionization potentials of 29 atoms (up to Cu inclusive) were found experimentally from spectra [1, 2]. Highly reliable data were obtained only for the first 20 atoms. Only approximate estimates of several ionization potentials were obtained for the other atoms. Energies of atoms and ions that were

[1] To whom any correspondence should be addressed.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

calculated by us using the HF approximation were compared with the experimental values using the first 29 atoms as examples. This enabled the accuracy of the energies of atoms and ions given by the HF method to be evaluated.

Table. Energies (in at. units) of ground states of neutral atoms from H to Cu and their first two ions calculated in the algebraic approximation of the Hartree–Fock method compared with the experimental values

n	$-E_{RHF}$	Δ%	n	$-E_{RHF}$	Δ%	n	$-E_{RHF}$	Δ%
	H			**He**			**Li**	
1	0,500000	–0,05	2	2,861679	0,49	3	7,432726	0,60
			3	2,000000	–0,01	4	7,236415	0,59
						5	4,500000	–0,002
	Be			**B**			**C**	
4	14,57302	0,65	5	24,52906	0,52	6	37,68861	0,44
5	14,27739	0,34	6	24,23757	0,47	7	37,29222	0,39
6	13,61129	0,33	7	23,37599	0,22	8	36,40849	0,37
	N			**O**			**F**	
7	54,40093	0,38	8	74,80939	0,40	9	99,40934	0,39
8	53,88800	0,35	9	74,37260	0,31	10	98,83172	0,33
9	52,81579	0,32	10	73,10019	0,29	11	97,60897	0,27
	Ne			**Na**			**Mg**	
10	128,5470	0,21	11	161,8589	0,35	12	199,6146	0,34
11	127,8178	0,17	12	161,6769	0,34	13	199,3718	0,33
12	126,3721	0,30	13	159,9973	0,31	14	198,8308	0,32
	Al			**Si**			**P**	
13	241,8767	0,34	14	288,8543	0,34	15	340,7187	0,35
14	241,6746	0,33	15	288,5731	0,34	16	340,3497	0,35
15	241,0307	0,32	16	287,9958	0,33	17	339,6449	0,34
	S			**Cl**			**Ar**	
16	397,5048	0,38	17	459,4820	0,41	18	526,8175	0,43
17	397,1731	0,37	18	459,0485	0,40	19	526,2745	0,42
18	396,3327	0,37	19	458,2264	0,39	20	525,3043	0,42
	K			**Ca**			**Sc**	
19	599,1647	0,46	20	676,7581	0,49	21	759,7357	0,41
20	599,0175	0,46	21	676,5700	0,48	20	759,5391	0,40
21	597,8916	0,45	22	676,1543	0,48	19	758,9808	0,42
	Cr			**Co**			**Ti**	
24	1043,356	0,62	27	1381,414	0,82	22	848,4059	0,50
23	1043,139	0,62	26	1381,128	0,82	21	848,2033	0,52
22	1042,577	0,62	25	1380,423	0,83	20	847,5563	0,54
	Mn			**Ni**			**V**	
25	1149,866	0,68	28	1506,870	0,86	23	942,8843	0,56
24	1149,649	0,67	27	1506,568	0,87	22	942,6707	0,55
23	1149,109	0,67	26	1506,030	0,86	21	941,9816	0,57
	Fe			**Cu**				
26	1262,443	0,67	29	1638,963	0,92			
25	1262,213	0,67	28	1638,694	0,92			
24	1261,564	0,66	27	1638,084	0,91			

n – the number of electrons in an atom or ion.
E_{RHF} is the energy calculated by the Roothaan–Hartree–Fock method (our calculation).
Δ% – $(E_{RHF} - E_{EXP})/E_{EXP}$, in %.

2. Calculation of energies in the algebraic approximation on the HF method

Energies of neutral atoms from He to Xe that were calculated with high accuracy in the framework of Roothaan–Hartree–Fock atomic theory (Roothaan–Bagus method [5]) [7] were reported. This method is based on the formula for the energy of an atom in the central field approximation in which integration over angular variables is carried out. The radial parts of orbitals are represented as expansions in basis functions [atomic orbitals (AO)]. Solving the HF equations in the algebraic approximation resulted in the solution of two interrelated problems, i.e., solution self-consistent field equations in generalized form into eigen values and calculation of optimal values of AO. In the program for solving SCF equations, the cyclic Roothaan method is used; then, if the process of reaching self-consistency diverges, the steepest descent method that is based on gradient and has a wider domain of convergence is employed. To optimize the orbital exponents AO, the direct optimization methods (the zero-order methods), for example, the Powell conjugate direction method [9], are commonly used. However, the convergence of these methods is slow and they provide limited accuracy of the optimized parameters. It is more promising to apply the second-order minimization methods that were described before [7]. Necessary condition for an energy minimum determines the rigorous criterion for the completion of calculation in such algorithms. A multistep scheme for optimizing the exponents that allows us to perform optimization with a high accuracy was used in the program. The resulting calculations exceeded all known calculations in the HF algebraic approximation with respect to the accuracy of the virial theorem (10^{-15}-10^{-17}). It was shown that energies corresponding to the HF-Iimit could be obtained in the framework of the algebraic method [7]. The radial parts of AO calculated in analytic form can be multiplied by the corresponding spherical functions, and the orbitals obtained can be used to solve the equations of perturbation theory in the HF approximation. It is precisely this approach that was implemented in the calculations of polarizability [6].

3. Results

Due to the comparison of the theoretically calculated by the HF method energies of atoms from H to Cu and of all their ions the authors got the results characterizing the accuracy of the calculated values. For atoms ($1 \leq Z \leq 20$) the error of theoretically obtained values of energy by the HF method is only 0.3%-0.5%. For the isoelectronic series of Sc, Ti, V error of experimental calculations is around 0.6%. However, it starts to grow, and for Ni and Cu atoms is up to 1%. At the same for such atoms the accuracy of experimental data, used for comparison, falls.

4. Conclusions

The results presented in this paper show that the use of the HF method in the calculation of atom and ion energy is quite effective. The error of the theoretical calculations, not exceeding 1%, taking into account the uncertainty of the experimental data, allows to confirm the correctness of the approximations, that compile the base of the Hartree–Fock method.

References

[1] Lide D R 2004 *Handbook of Chemistry and Physics* (New York: CRC Press) p 2475
[2] Moore C E 1970 *Natl. Stand. Ref. Data* **34** 22
[3] Yutsis A P 1978 *Theory of Polyelectronic Atoms. Selected Works* (Vilnius: Mokslas)
[4] Hartree D R 1957 *The Calculation of Atomic Structure* (New York: J. Wiley)
[5] Roothaan C C J and Bagus P S 1963 *Methods in Computational Physics* (New York: Academic Press) **2** 47-94
[6] Eremkin I N and Malykhanov Yu B 2011 *Zh. Prikl. Spektrosk*. **74** (3) 325-332
[7] Malykhanov Yu B, Gorshunov M V, Evseev S V, Eremkin I N and Chadin R M 2013 *Opt. Spektrosk.* **114** (3) 355-362
[8] Malykhanov Yu B and Gorshunov M V 2013 *Zh. Prikl. Spektrosk*. **80** (5) 649-654
[9] Koga T, Watanabe S, Kanayama K, Yasuda R and Thakkar A J 1995 *J. Chem. Phys.* **103** (8) 3000-3005